SCIENCE FOR GLASS PRODUCTION

EFFECT OF TWO-STAGE PREMIXING ON CAKING IN BIALKALINE GLASS BATCHES FOR INSULATOR GLASS

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Caking is investigated in a bialkaline glass batch for electroinsulating glass stored in the cold. Technological regimes of two-stage premixing of sand with water and alkali-bearing components in batch preparation are proposed. The effect of the temperature of water and premixing schedules on batch caking is analyzed, and technological recommendations are issued to optimize the two-stage premixing of batch.

Among the main reasons for hardened glass particles breaking during the production of high-voltage electric insulators are glass melt defects, in particular, its chemical heterogeneity. Therefore, the quality of insulator glass batch has a significant influence on the hardening process and the quality of glass parts. The use of high-quality materials is a necessary but not a sufficient condition for producing high-quality batch. The processes of mixing batch components, its transportation, and storage to a great extent affect the glass melt quality.

When prepared batch is stored for a long time, especially in large containers and at below-zero temperatures, it tends to cake and after reloading becomes clotted and stratified, which disturbs its homogeneity. The process of preparing batch as a homogeneous mixture of components to a large extent is determined by their optimum mixing. Batch components have different granulometric composition, specific weight, and chemical nature; therefore, when then are moistened inside a mixer and the grains of some components are smoothed by the grains of other (more disperse) components they start reacting with water and each other and may form clots; furthermore, in reloading and storage they may form large-size conglomerates, which frequently make the batch heterogeneous. Consequently, caking in a batch is inadmissible, since the clots are sure to have a different composition from the rest of the batch [1 – 3].

Caking in a glass batch is related to the presence of components that are chemically active with respect to water and to each other. Their moistening and mixing generates various physicochemical processes: dissolution, chemical reactions, formation of crystal hydrates, thermal phenomena. This is primarily true of the alkali-bearing batch components, i.e., soda ash, potash, and sodium sulfate that tend to generate thermally unstable crystal hydrates with different water content [1]. Under the traditional moistening of a prepared batch in the industry the above-mentioned hygroscopic components become centers of clot formation, and when the batch is stored in a cold humid space, caked and consolidated clots may lead to the chemical heterogeneity of this batch.

We have analyzed a method for decreasing clotting in batches for bialkaline electroinsulating glass by preliminary mixing its alkali components with moistened sand.

The batch contains three alkali-bearing components: Na_2CO_3 (technical soda ash from the Krymsoda Company), K_2CO_3 (technical potash from the Pikalevskii Works in Leningrad Region), and Na_2SO_4 (technical sodium sulfate from the Konstantinovskii Works in Donetsk Region). Their weight ratio in a batch is 15 : 5 : 1, respectively. The sizes of alkali-bearing grains are not more than 0.9 mm (soda, sulfate) or 1.4 mm (potash). The batch in the industrial conditions is prepared by the dry method with moistening up to 6%. The traditional mixing cyclogram includes preliminary mixing of quartz sand with water (2 min), then feeding the other components into the mixture (0.5 min), and their final mixing (3.5 min). The total mixing duration is 6 min.

It is known that preliminary mixing of sand with water facilitates a homogeneous distribution of moisture in quartz sand, which is the largest (by weight) batch component and decreases dusting and losses of the lightest and most finely dispersed alkali-bearing components.

The mixing schedules considered imply adding one or several of the specified alkali-bearing components, including potash dissolved in water, which is the most hygroscopic component, to the premixing cyclogram (sand + water).

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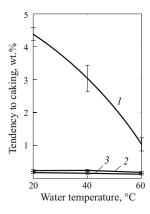
Fig. 1. Tendency to caking in batches after mixing with water at different temperatures: *1*) without premixing with alkali components (schedule 0); *2* and *3*) with premixing (schedules 3 and 5, respectively).

In the laboratory conditions the batch was prepared manually from standard materials according to the formula following preset cyclogram. The prepared batch was aged for 3 days in cold (+ 5°C), after which it was tested for clotting (sifted for 2 min through a sieve with holes 2 mm in diameter, after which the sieve residue was weighed and its percentage in the batch sample calculated).

In mixing batch components we observe the formation and disintegration of conglomerates, especially in the first moments, which is primarily related to the chemical reaction between soda and water and the formation of crystal hydrates.

It is known [2] that soda at a temperature below 32°C reacts with water and forms crystal polyhydrates (deca- and heptahydrates), whereas soda monohydrate is formed only at a temperature above 35°C, that is, around 20°C soda presumably binds the entire moisture in the batch, whereas the rest of the batch is being mixed as a dry mixture, which impairs the batch homogeneity.

If freshly prepared batch is sifted though a sieve, nearly all agglomerates (accretions) disintegrate in grating against the metal sieve mesh, since these new formations (based on soda decahydrate) are not strong. Potash is possibly contained in these agglomerates as well (introduced into the batch in the sesquihydrate state); it actively absorbs soda and is partly dissolved in it (becomes soaked). Thus, soda and potash (especially potash) actively react with water in the course of mixing of a moistened batch.

The formation of clots in a batch prepared according to the traditional technology and stored at low temperatures may be caused by a protracted contact between the hygroscopic compounds (crystal hydrates of soda, potash, and sodium sulfate which at a temperature below 32°C also forms a decahydrate, although its effect in the batch is insignificant due to its low content). The averaged clot content in the traditionally prepared batch is equal to 4.4%.

It should be noted that the dissolution process is endothermic, whereas the hydration process (formation of crystal hydrates) is exothermic; therefore, freshly formed soda crystal hydrates easily become "eroded" and lose part of their constitution water, i.e., disintegrate [2]. The total thermal effect of carbonates reacting with water can be either negative or positive, depending on which of the above processes prevails. For instance, in the initial moments of alkaline carbonates reacting with water they become dissolved and form a supersaturated solution, since the amount of water is insufficient for dissolving all carbonates and their solubility is considerable. Thus, alkali carbonates at the start of moistening alkali actively absorb heat, and the higher the water temperature, the more intense is the dissolution process. As for the batch quality, finely dispersed soda at the initial moments of mixing should be quickly fixed with water whose temperature ought to be high to ensure the maximal dissolution and subsequent crystallization.

Supersaturated solutions of alkali carbonates and sulfates immediately crystallize and form different crystal polyhydrates while releasing heat. The larger the quantity of water molecules retained by the carbonates and sulfates in the batch, the drier and the less homogeneous is the batch. Therefore, in moistening a batch one should strive to prevent the formation of crystal polyhydrates, which can be avoided at temperatures above 35°C, when soda decomposes to its monohydrate.

For preliminary mixing sand with water, the water temperature was raised to 60°C without changing the traditional mixing cyclogram and then the clot content in the batch was determined.

It can be seen (Fig. 1) that the clot content in the batch after its storage in the cold decreases (on the average by 40%) with water temperature growing from 20 to 40°C and at 60°C the clot content decreases to less than one-fourth. In fact, within the temperature interval of 40 – 60°C soda deca- and pentahydrates decompose to monohydrate, which becomes dehydrated at a temperature above 100°C. A clot content in the batch equal to about 1% (using water of temperature 60°C) presumably indicates a certain decrease in the temperature of the mixture by the end of mixing. Clearly, the actual temperature of the moistened batch changes in mixing (it first grows and then decreases), however, the initial temperature of the interaction between the alkali components and water is responsible for the moisture distribution between the other batch components.

Therefore, the water temperature for premoistening sand should be at least 60°C; in that case subsequent processes of dissolution, hydration, and dehydration of alkali-bearing components occur at higher temperatures and these components are retained in the batch to a maximum extent, whereas mixing other moistened components ensures minimal clotting. However, the currently adopted technology of batch preparation involving premixing of sand and water even under an increased temperature of water does not totally prevent the formation of clots in storage. Therefore, we propose a technology of two-stage premixing of moistened sand with alkali components:

sand + water (2 min) + alkali components (2 min).
first stage   second stage

The separate premixing technology is based on the fact that in the case of simultaneous mixing of sand, water, and alkali components, the latter are sure to actively react with

water, while the sand remains dry. The newly proposed schedule allows the premixing duration to be extended 2 times (from 2 to 4 min), but mixing moistened sand and the alkali-bearing components (whose weights differ more than 4 times) for less than 2 min is insufficient. The technological regimes of two-stage premixing of the bialkaline batch components are given in Table 1.

The batch components premixed according to schedules 1 – 5 were subsequently mixed with the remaining batch components for 3.5 min. Prepared batches were stored for 2 days in humid conditions at a temperature of + 5°C and then sifted through a No. 02 sieve. The estimated clot content of the batches is listed below.

Clotting in batch premixed by two-stage mixing at 20°C

Premixing schedule	Content of clots in batch sample, wt.%
0	4.40 ± 0.20
1	1.26 ± 0.05
2	0.46 ± 0.02
3	0.25 ± 0.02
4	0.25 ± 0.02
5	0.20 ± 0.02

It can be seen that premixing soda with moist sand (two-stage premixing schedule 1) decreases the clot content in the batch 3.5 times and premixing with potash (schedule 2) makes it nearly 10 times less than in the conditions currently adopted in the industry (schedule 0). This shows that potash has a critical effect on clot formation in a batch (although its weight content is one-third of that of soda) and needs to be premixed with moist sand.

When moist sand in the second stage is jointly premixed with soda and potash (schedule 3) or with the three alkali-bearing components (schedule 4), the clot content in the batch is nearly 20 times lower than in the case of premoistening sand (schedule 0). Comparing the clot content in batches premixed according to schedules 3 and 4, it can be stated that adding sodium sulfate at the second stage has little effect on clotting, since its weight content in the mixture is insignificant (soda : sulfate = 15 : 1). Thus, the main batch components that significantly affect the caking process are potash and soda.

Schedule 5 of two-stage premixing of batch components implies a complete dissolution of a potash portion in a portion of batch-moistening water (which corresponds to the solubility of 80 g K_2CO_3 at 20°C, complete dissolution) and then using the resulting solution for 2 min to moisten the sand. The clot content of the batch premixed with a potash solution (schedule 5) is 20 % lower than in premixing with dry potash (schedule 3), i.e., using the potash solution for premoistening sand and then mixing the latter with soda is the optimum premixing schedule to achieve the minimal clotting of the batch (0.2%).

As the temperature of water used for two-stage premixing increases to 40 – 60°C, the clot content in the batch decreases even more and reaches 0.15% for schedule 5 (60°C, Fig. 1).

TABLE 1

Schedule	First stage		Second stage	
	components	duration, min	components	duration, min
0	Sand + water	2	–	–
1	The same	2	Soda	2
2	"	2	Potash	2
3	"	2	Soda + potash	2
4	"	2	Soda + potash + sulfate	2
5	Sand + potash solution	2	Soda	2

Thus, premixing moistened sand separately with potash and with soda under a water temperature equal to 20°C indicates the dominant effect of potash on clot formation in the batch. Joint premixing of moist sand with soda and potash significantly decreases the clot content of the batch after storage in cold under humid conditions (more than 20 times). Preliminary dissolution of potash at an increased temperature (40 – 60°C) and subsequent two-stage mixing first with sand and then with soda virtually eliminates clots in the batch. This is presumably due to eliminating the main reason for clot formation in a bialkaline batch, namely, hygroscopic potash particles that are centers of reactions with soda and other carbonates when a moist batch is stored.

In the case of two-stage premixing of sand with alkali-bearing components, it is not necessary to use sodium sulfate, as it has virtually no effect on clot formation due to its low content in the batch. A uniform distribution of the potash solution between sand grains (the first stage of premixing) and a subsequent uniform distribution of soda particles (the second stage) facilitate the formation of a homogeneous mixture of batch components. An increase in the temperature of water (solution) used to moisten the batch in mixing leads to the thermal decomposition of soda, potash, and sodium sulfate crystal hydrates and the release of water that serves to fix the rest of the batch components.

The optimum regime of preliminary mixing of quartz sand with alkali-bearing components is two-stage mixing of sand with a potash solution and then with soda at a temperature of 40 – 60°C. According to the proposed schedule, the time of mixing the batch components is somewhat extended compared to the schedule currently accepted in the industry (from 6 to 8 min), but the batch quality improves significantly.

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